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(54) **Process for preparation of a plastic vessel having an oriented coating.**

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## Description

## Background of the Invention

## (1) Field of the Invention

5 The present invention relates to a process for the preparation of a plastic vessel having an oriented coating in which such properties as the adhesion of a vinylidene chloride copolymer coating to a substrate, the whitening resistance and the gas barrier property are highly improved, and a process for the preparation thereof.

## (2) Description of the Prior Art

10 Plastic bottles formed by melt-extruding a thermoplastic material such as a polyolefin and hollow-molding (blow-molding) the melt are used in various fields instead of glass bottles because they are lighter in the weight than glass bottles and are excellent in the impact resistance.

15 General-purpose plastics such as polyolefins are excellent in the moisture resistance and sanitary characteristics, but they have a relatively large oxygen permeation coefficient and permeation of oxygen through the vessel wall cannot be neglected. Therefore, these plastic materials are not suitable for the production of vessels to be used for preserving foods for a long time or cosmetic vessels for which a high perfume-retaining property is required.

20 As vessels in which this defect is eliminated, there have already been developed plastic bottles comprising a resin excellent in the oxygen barrier property as a vessel wall-constituting component. Among melt-extrudable thermoplastic resins available at the present, a saponified ethylene-vinyl acetate copolymer (ethylene-vinyl alcohol copolymer) is most excellent in the oxygen barrier property. However, this saponified copolymer is poor in the moisture resistance, that is, the water vapor barrier property, and in this saponified copolymer, the oxygen permeation coefficient tends to prominently increase with increase of the humidity. Therefore, when this saponified copolymer is practically used for the production of plastic bottles, the saponified copolymer is sandwiched with a moisture-resistant resin such as a polyolefin and the resulting laminate is used, which is very troublesome.

25 Plastic bottles formed by viaially draw-blow-molding a parison of a polyester composed mainly of ethylene terephthalate units are now used as packaging vessels for beverage or beer. Plastic bottles of this type are light in the weight and excellent in the impact resistance, but they are defective in that the life is considerably shorter than the life of glass bottles.

30 It is known that a vinylidene chloride copolymer is excellent in the barrier property to various components. For example, the specification of U.S. Patent No. 3,922,451 teaches that when a latex of a vinylidene chloride copolymer is applied to the inner surface of a metal vessel or plastic vessel and the latex is dried under certain conditions, a protective coating excellent in the continuity and adhesion to the substrate can be formed.

35 However, as the result of research made by us, it was found that the adhesion of a coating of a vinylidene chloride copolymer applied in the form of a latex to plastic substrates is still insufficient and involves a problem. More specifically, when a content is stored for a long time or the vessel is attacked by heat, pressure or a chemical, such a trouble as peeling of the vinylidene chloride copolymer coating from the plastic substrate or whitening of the coating per se is readily caused and the intended improvement of the gas barrier property cannot be attained.

40 U.S. Patent No. 4,127,633 discloses a process for the preparation of coated oriented plastics vessels, which comprises coating an aqueous latex (or dispersion) of a vinylidene chloride copolymer on at least one surface of a preform composed of a molecularly orientable thermoplastic resin and drying the coated latex to form a coated structure. The coated structure is subjected to a draw-molding operation at a temperature higher than the glass transition temperature of the vinylidene chloride copolymer but lower than the melting point of the vinylidene chloride copolymer to form the coated structure into a vessel shape while drawing the coated layer.

45 We have found that if a coating of a vinylidene chloride copolymer formed on an amorphous polyethylene terephthalate substrate is molecularly oriented under specific conditions, the adhesion of the coating to the plastic substrate is prominently improved and the whitening resistance and gas barrier property are further enhanced.

50 According to the present invention there is provided a process for the preparation of coated oriented plastic vessels, which comprises coating an aqueous latex of a vinylidene chloride copolymer on at least one surface of a bottomed parison composed of amorphous polyethylene terephthalate, drying the coated latex to form a coated structure provided with a surface coating layer on a polyethylene terephthalate substrate and subjecting the coated structure to biaxial draw-blow-molding at a temperature at which the draw-molding of the coated structure is possible and draw-molding the coated structure at a temperature higher than the glass transition temperature of the vinylidene chloride copolymer but lower than the melting point of the vinylidene chloride copolymer to form the coated structure into a shape of a vessel while drawing the coating layer so that the coating layer of the vinylidene chloride copolymer has a molecular orientation, characterized in that the biaxial draw-blow-molding is carried out under conditions such that the temperature of the coated structure is lower by at least 5°C than the average temperature of the polyethylene terephthalate substrate and the resultant coating layer has a molecular orientation such

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that the sum of the two-dimensional orientation coefficients ( $l + m$ ) in the axial direction and circumferential direction is at least 0.03 as measured by polarised light fluorometry and the coating layer is not substantially peeled in the low-temperature burst test conducted at  $-5^{\circ}\text{C}$ .

These and other features of the present invention are disclosed in more detail in the following description and accompanying drawings.

### Brief Description of the Drawings

Fig. 1 is a partially sectional view showing one embodiment of the coated plastic vessel prepared according to the present invention.

### Detailed Description of the Preferred Embodiments

Referring to Fig. 1 of the drawings, a coated plastic bottle 1 comprises a circumferential wall portion 2 having a circular or ellipsoidal section, a mouth portion 3 contiguous integrally to the circumferential wall portion 2 and a bottom portion 4 contiguous to the lower end of the circumferential wall portion 4. The entire wall of the bottle comprises a substrate 5 of a melt-modable plastic material and a coating layer 6 of a vinylidene chloride copolymer formed on the surface of the substrate 5. The substrate and coating layer are formed into a shape of a bottle by biaxial draw-blow-molding. This coating layer 6 may be formed on both the surfaces of the substrate 5 as shown in Fig. 1, or it may be formed only on the inner surface or outer surface of the substrate 5.

As pointed out hereinbefore, one of important features of the present invention resides in the finding that when the coating layer 6 of a vinylidene chloride copolymer is molecularly oriented so that the in-plane orientation coefficient ( $l + m$ ) is at least 0.03, especially at least 0.05, the adhesion of the coating layer 6 to the plastic substrate 5 is prominently improved even under very severe conditions.

It is known that a vinylidene chloride copolymer is excellent in the barrier property to various gases such as oxygen, carbon dioxide gas and water vapor. However, hot molding of this copolymer is very difficult and when the copolymer is used for formation of a coating, the copolymer should be handled in the form of an aqueous latex.

In order to shape a resin applied in the form of latex particles into a dense and continuous coating film, it is ordinarily necessary to heat the applied latex resin particles at a temperature higher than the film-forming temperature inherent to the latex resin particles. It is considered that from this viewpoint, the specification of the above-mentioned U.S. patent No. 3922451 specifies that the latex coating should be dried at a temperature higher than  $110^{\circ}\text{C}$ .

Indeed, the coating formed under this drying condition is seemingly continuous and adheres closely to the plastic substrate. However, when the coating is dipped in an alkaline aqueous solution or benzene, or when the content in the vessel is frozen and the vessel is swollen, the coating of the vinylidene chloride copolymer is likely to peel off from the plastic substrate. Furthermore, the coating of the vinylidene chloride copolymer tends to peel very easily on contact with various chemicals or hot water. It is considered that in a coating film formed by heating latex particles of a vinylidene chloride copolymer, the particles are aggregated with one another to some extent to form a dense structure but an interface called "stone wall structure" is still left among the particles and troubles such as the above-mentioned peeling and whitening are caused because of the presence of this interface.

In the present invention, by molecularly orienting the coating of the vinylidene chloride copolymer at a high ratio, foreign substances present in the interface among particles, such as an emulsifier and a dispersant, are pushed out, with the result that the denseness and adhesion of the coating are prominently improved.

The sum of two-dimensional orientation coefficients or the in-plane orientation coefficient ( $l + m$ ) referred to in the instant specification and appended claims is a value determined according to the polarized light fluorometry, as described, for example, by Mr Yasunori Nishijima in Polymer, Vol. 15, No. 175, page 868 (1966) published by the Japanese Association of Polymers, and is quantitatively given by the following formula:

$$I_{\parallel}(\omega) = K\phi(l\cos^4\omega + m\cos^4\omega + \frac{3}{8}n)$$

wherein  $I_{\parallel}(\omega)$  stands for the intensity of the polarized light component of the fluorescence emitted from a thermoplastic resin as the sample, the mark  $\parallel$  indicates that the vibration direction of the incident polarized light is in parallel to the direction of the measured polarized light,  $\omega$  stands for the rotation angle of the sample to the vibration direction of the above-mentioned polarized light,  $K$  stands for the maximum excitation probability attainable when the molecular axis of the sample is in parallel to the vibration direction of the excited fluorescence,  $\phi$  stands for the molecular fluorescent shrinkage, and  $l$  stands for the ratio of orientation of the molecules in one optional direction (axial direction) in the plane of the wall of the final formed vessel,  $m$  stands for the ratio of orientation of the molecule in the direction (circumferential direction) rectangular to the direction  $l$ ,  $n$  stands for the ratio of non-orientation in the plane and the relation of  $l + m + n = 1$  is established.

When the in-plane orientation coefficient ( $l + m$ ) of the coating layer of the vinylidene chloride copolymer in the final vessel is smaller than 0.03, the intended improvements of the adhesion of the coating layer to the plastic substrate of the vessel, the whitening resistance and the gas barrier property cannot be attained. According to the present invention, by giving the above-mentioned orientation also to the coating layer, even if the vessel is subjected to the low-temperature burst test at  $-5^{\circ}\text{C}$ , peeling of the coating layer from the plastic substrate can be prevented. Furthermore, as shown in Examples given hereinafter, even if the vessel is dipped in an alkaline aqueous solution or an organic solvent such as benzene for a long time, the adhesion of the coating layer to the substrate is hardly degraded.

Since the coating layer of the vessel of the present invention is densified by the above-mentioned molecular orientation, whitening is hardly caused even on contact with various chemicals or hot water, and the carbon dioxide gas permeation coefficient is reduced to about  $\frac{1}{2}$  of the carbon dioxide gas permeation coefficient of the unoriented coating layer when the comparison is made based on the same thickness. Thus, the gas barrier property is prominently improved according to the present invention.

The bottomed parison, (preform) that is used in the present invention is obtained from a molecularly orientable, hot-moldable thermoplastic resin by any optional known hot-molding means. For example, a bottomed parison can be obtained by extruding the above-mentioned resin in the form of a cylinder, pinching off the cylinder by a split mold and performing preliminary blow-molding. Moreover, a bottomed parison for biaxial draw-blow-molding can be obtained by injection molding of the above-mentioned resin.

The resin to be used for formation of the parison is amorphous polyethylene terephthalate. The plastic parison may have a single-layer structure, or it may have a laminate structure including at least two layers, which is prepared, for example, by co-melt-extrusion.

At least one surface of the plastic parison is coated with an aqueous latex of a vinylidene chloride copolymer. A copolymer comprising vinylidene chloride as main structural units and at least one comonomer selected from acrylic and methacrylic monomers, vinyl aromatic monomers such as styrene and vinyl toluene, vinyl esters such as vinyl acetate and vinyl propionate, diolefins such as butadiene and isoprene, and methyl vinyl ether, glycidyl allyl ether, vinyl chloride, trichloroethylene, tetrachloroethylene, vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, maleic anhydride, fumaric acid, vinylsuccinic acid imide and vinyl pyrrolidone, is used. As preferred examples of the acrylic and methacrylic monomers, there can be mentioned acrylic acid, acrylonitrile, acrylamide, methyl acrylate, ethyl acrylate, methyl  $\alpha$ -chloroacrylate, propyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, cyclohexyl acrylate, glycidyl acrylate, 2-hydroxyethyl acrylate, acrylic monoglyceride, phenyl acrylate, methacrylic acid, methacrylonitrile, methacrylamide, methyl methacrylate, amyl methacrylate, glycidyl methacrylate, methacrylic monoglyceride, 2-hydroxypropyl methacrylate,  $\beta$ -methoxyethyl methacrylate,  $\beta$ -aminoethyl methacrylate and  $\gamma$ -N,N-diethylaminopropyl methacrylate.

An aqueous copolymer latex having a solid concentration of 20 to 65% and a viscosity of 3 to 500 cps is preferably used.

A known coating method such as dip coating, spray coating, brush coating, roller coating, flow coating, electrostatic coating, centrifugal coating, flow cast coating, electrophoretic coating or a combination thereof may be adopted for coating the above-mentioned latex on the plastic parison. The coating may be conducted only once, or a multistage coating method in which the coating is carried out at least two times may be adopted. If necessary, in order to improve the wettability characteristic of the plastic parison, a preliminary treatment such as a treatment with an anchoring agent, a corona discharge treatment, a surface active agent-coating treatment or a chemical etching treatment may be performed before the coating operation. Furthermore, a conductive treatment may be carried out so as to render the substrate electrically conductive.

It is preferred that a coating layer of the above-mentioned copolymer be formed on both the surfaces of the plastic parison. In order to prevent intrusion of gases contained in air, it is sufficient if the coating layer is formed on the surface to be formed into the outer surface of the final vessel, and in order to prevent escape of a gas or perfume from the content, it is sufficient if the coating layer is formed on the surface to be formed into the inner surface of the final vessel.

The copolymer that is used in the present invention is excellent in the combination of the oxygen barrier property and the water vapor permeability, and the humidity dependency of the oxygen barrier property is very small. Accordingly, if only a very thin layer of the copolymer is formed on the plastic bottle substrate, there can be obtained an excellent barrier property to various gases, and satisfactory results can be obtained if the thickness of the copolymer layer formed on the final vessel is 0.1 to 40  $\mu$ , especially 0.5 to 30  $\mu$ .

The coated copolymer is dried at a temperature of 20 to  $150^{\circ}\text{C}$ , especially 40 to  $108^{\circ}\text{C}$ , for 2 seconds to 100 hours, though the drying conditions differ to some extent according to the thickness of the coating.

In the present invention, even if the temperature of the coating layer of the vinylidene chloride copolymer is not elevated to a high level, the denseness and adhesion of the coating layer can be enhanced by the molecular orientation, and therefore, deterioration due to thermal decomposition of thermal degradation, as caused when a resin layer is heated at a high temperature, can be reduced. This is another advantage attained in the present invention.

According to the present invention, the resulting coated structure is subjected to biaxial draw-blow molding at a temperature higher than the glass transition temperature of the vinylidene chloride copolymer

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but lower than the melting point of the vinylidene chloride copolymer, at which temperature draw-molding of the above-mentioned thermoplastic resin is possible, whereby the coated structure is formed into a shape of a vessel while drawing the coating layer.

The glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) of the vinylidene chloride copolymer differ according to the kind and amount of the comonomer. However, the molding temperature is ordinarily in the range of from  $-25$  to  $190^\circ\text{C}$ , especially from  $-20$  to  $180^\circ\text{C}$ . If the molding temperature is too low and below the above range, the drawing operation becomes difficult because of breakage of the coating, and if the molding temperature is too high and exceeds the above range, it is impossible to set the molecular orientation caused by drawing in the coating layer. Furthermore, in order to draw the coating layer, the thermoplastic resin as the substrate should also be drawn. From this viewpoint, it is important that the molding temperature should be within the range of temperatures at which draw-molding of the thermoplastic resin as the substrate is possible.

Since the coating of the vinylidene chloride copolymer used in the present invention can be molecularly oriented at a relatively low temperature by drawing, as pointed out hereinbefore, it is possible to perform draw-molding in such a state that a temperature difference resides between the outer surface. When draw-molding is carried out under such conditions that the temperature ( $T_o$ ) of the outer surface of the coating layer is lower by at least  $5^\circ\text{C}$  than the average temperature ( $T_s$ ) of the resin substrate, an effective molecular orientation can be imparted to the coating layer while preventing deterioration thereof.

In order to maintain the parison at the above temperature, a preliminary heat treatment and, if necessary, a cooling treatment may be performed.

Draw-molding of the parison coated with the vinylidene chloride copolymer may be carried out under known conditions if the above requirements are satisfied. Namely, biaxial draw-blow molding is carried out under temperature conditions causing the molecular orientation by drawing of the plastic substrate and coating layer.

For biaxial draw-blow-molding, a parison is mechanically drawn in the axial direction in a split mold, and simultaneously, a fluid is blown into the parison or preform to expand and draw the parison in the circumferential direction. Drawing in the axial direction is accomplished by pushing a drawing rod in the bottom parison.

The present invention will now be described in detail with reference to the following Examples that by no means limit the scope of the invention.

Incidentally, in the Examples, the solvent resistance, chemical resistance (alkali resistance), hot water resistance, low-temperature ( $-5^\circ\text{C}$ ) burst characteristic, oxygen permeability, carbon dioxide gas permeability, water vapor permeability, oxygen permeation coefficient, carbon dioxide gas permeation coefficient and water vapor permeation coefficient were determined and calculated according to the following methods.

### (i) Solvent Resistance:

A square test piece having a size of  $2\text{ cm} \times 2\text{ cm}$  was cut out from the barrel portion of the vessel to be tested, and the test piece was immersed in benzene for 30 minutes, 1 hour or 24 hours. The solvent resistance was evaluated by the observation with the naked eye according to the following rating.

X: whitening and peeling were caused

$\Delta$ : peeling was caused though whitening was not caused

O: whitening or peeling was not caused.

### (ii) Chemical Resistance:

A test piece was prepared as described in (i) above, and the test piece was immersed in an aqueous solution containing 10% by weight of caustic soda for 5 minutes, 10 minutes, 1 hour or 24 hours. The chemical resistance was evaluated by the naked eye observation according to the following rating.

X: browning and peeling were caused

$\Delta$ : browning was caused though peeling was not caused

O: browning or peeling was not caused.

### (iii) Hot Water Resistance:

A test piece was prepared as described in (i) above, and the test piece was boiled for 30 minutes in a thermostat hot water tank maintained at  $95^\circ\text{C}$ . The test piece was taken out from the tank and the whitening degree of the test piece was judged by two experts based on the naked eye observation.

O: the two experts judged that no whitening was caused

$\Delta$ : one expert judged that no whitening was caused but the other expert judged that whitening was caused

X: the two experts judged that whitening was caused

### (iv) Low-Temperature Burst Characteristic:

The vessel to be tested was filled with an aqueous solution containing 10% by weight of sodium chloride, which was maintained at  $-5^\circ\text{C}$ . After it was confirmed that the vessel was cooled to  $-5^\circ\text{C}$ , the above aqueous solution was further supplied into the vessel at a compression rate of  $15\text{ Kg/mm}$  to burst the

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vessel. The burst vessel was observed and evaluation was conducted according to the following rating.

○: peeling or whitening was not caused

△: peeling was not caused but whitening was caused

X: peeling was caused

## 5 (v) Oxygen Permeability (QO<sub>2</sub> at 20°C and 0% RH):

A sheet having a predetermined size was cut out from the barrel portion of the vessel to be tested, and was attached to a gas permeation tester (supplied by Toyo Tester Kogyo K.K.). The sample was secured between two chambers, and the pressure was reduced below 10<sup>-2</sup> mmHg in one chamber (low pressure side) and the atmosphere of the other chamber (high pressure side) was substituted with oxygen dehumidified with calcium chloride so that the pressure in the chamber was 1 atmosphere. The increase of the pressure on the low pressure side was read by a recorder and the oxygen gas permeability was measured.

The measurement was carried out at 20°C, and the relative humidity was reduced to 0% by calcium chloride on the high pressure side.

## 15 (vi) Carbon Dioxide Gas Permeability (QCO<sub>2</sub> at 20°C and 0% RH):

The measurement was carried out in the same manner as described in (v) above by using carbon dioxide gas instead of oxygen.

## 20 (vii) Water Vapor Permeability (QH<sub>2</sub>O):

The water vapor permeability QH<sub>2</sub>O was carried out according to the method of JIS Z—0208 (Temperature: 40°C, relative humidity: 0 to 90%). A sheet having a predetermined size was cut out from the barrel portion of the vessel and was subjected to the measurement.

## 25 (viii) Calculation of Oxygen Gas Permeation Coefficient PO<sub>2</sub>, Carbon Dioxide Gas Permeation Coefficient PCO<sub>2</sub> and Water Vapor Permeation Coefficient PH<sub>2</sub>O of Vinylidene Chloride Copolymer Resin:

Since the values of QO<sub>2</sub>, QCO<sub>2</sub> and QH<sub>2</sub>O determined according to the above-mentioned methods were those of the composite system of the vinylidene chloride copolymer resin and the vessel substrate, the oxygen permeation coefficient PO<sub>2</sub>, carbon dioxide permeation coefficient PCO<sub>2</sub> and water vapor permeation coefficient PH<sub>2</sub>O of the vinylidene chloride copolymer resin coating at the above-mentioned temperature and relative humidity were calculated according to the following equations:

$$35 \quad PO_2 = \frac{(1.52 \times 10^{-15}) \times h}{\left( \frac{1}{(QO_2)} - \frac{1}{(QO_2)B} \right)} \quad [\text{cc} \cdot \text{cm} / \text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}],$$

$$40 \quad PCO_2 = \frac{(1.52 \times 10^{-15}) \times h}{\left( \frac{1}{(QCO_2)} - \frac{1}{(QCO_2)B} \right)} \quad [\text{cc} \cdot \text{cm} / \text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}],$$

and

$$50 \quad PHO_2 = \frac{(1 \times 10^{-4}) \times h}{\left( \frac{1}{(QHO_2)} - \frac{1}{(QHO_2)B} \right)} \quad [\text{g} \cdot \text{cm} / \text{m}^2 \cdot \text{day}]$$

where h stands for the thickness (μ) of the vinylidene chloride copolymer resin, (QO<sub>2</sub>) stands for the oxygen permeability [cc/m<sup>1</sup>·day·atm] of the composite system of the vessel substrate and coating layer, (QO<sub>2</sub>)B stands for the oxygen permeability [cc/m<sup>2</sup>·day·atm] of the vessel substrate, (QCO<sub>2</sub>) stands for the sum [cc/m<sup>2</sup>·day·atm] of the carbon dioxide gas permeability of the vessel substrate and the carbon dioxide gas permeability of the coating layer, (QCO<sub>2</sub>)B stands for the carbon dioxide gas permeability of the vessel substrate, (QH<sub>2</sub>O) stands for the sum [G/m<sup>2</sup>·day] of the water vapor permeability of the vessel substrate and the water vapor permeability of the coating layer, and (QH<sub>2</sub>O)B stands for the water vapor permeability of the vessel substrate.

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## Example

The inner or outer surfaces of preforms (bottomed parison) having an outer surface area of 130 cm<sup>2</sup>, a weight of 62.5 g and an average thickness of 3.60 mm and being composed of amorphous polyethylene terephthalate were separately dip-coated with a polyvinylidene chloride type resin latex (dispersion medium: water, solid concentration: 47% by weight, T<sub>g</sub>: 17°C, T<sub>m</sub>: 148°C) comprising 100 parts by weight of 83% by weight of vinylidene chloride, 14% by weight of methoxyethylmethyl acrylate and 3% by weight of methyl acrylate and 40 parts by weight of trichloroethylene, resulting in a coating amount as solids of 0.18 g and 0.22 g respectively, and the coated preform was dried at 70°C for 2 minutes. By using a known biaxial draw-blow-molding machine, the preform was heated for 20 seconds so that the maximum outer surface temperature was 130°C and the outer surface temperature at the blowing step was 117°C, and the preform was biaxially draw-blow-molded to obtain a biaxially drawn polyethylene terephthalate bottle having an inner capacity of 2000 cc and having the inner or outer surface coated with the vinylidene chloride copolymer. The bottle having the inner surface coated was designated as "bottle E1", and the bottle having the outer surface coated was designated as "bottle E2".

Uncoated polyethylene terephthalate bottles were obtained by subjecting an uncoated preform as described above to biaxial draw-blow-molding under the same conditions as described above, and the inner or outer surface of the bottle were separately dip-coated with the above-mentioned vinylidene chloride copolymer latex resulting in a coating amount of 1.18 g and 1.21 g respectively. The coated bottle was dried at 70°C for 2 minutes. The bottle having the inner surface coated was designated as "bottle F1" and the bottle having the outer surface coated was designated as "bottle F2".

With respect to each bottle, the organic solvent resistance, chemical resistance (alkali resistance), hot water resistance, low-temperature (-5°C) burst characteristic, oxygen permeability, carbon dioxide gas permeability and water vapor permeability were determined according to the methods described hereinbefore.

Incidentally, in order to calculate the gas permeation of the coating layer, the uncoated bottle was used for the measurement of the gas permeation coefficient.

The obtained results are shown in the Table.

TABLE

	Bottle			
	E1	E2	F1	F2
I + m				
<u>Organic Solvent Resistance</u>				
30 minutes	○	○	X	X
1 hour	○	○	X	X
24 hours	○	○	X	X
<u>Chemical Resistance</u>				
5 minutes	○	○	△	X
10 minutes	○	○	X	X
1 hour	○	○	X	X
24 hours	○	○	X	X
Hot Water Resistance	○	○	X	X
Low-Temperature Burst Characteristic	○	○	X	X
<u>Gas Permeation Coefficients of Coating Layer</u>				
PO <sub>2</sub>	1.0 × 10 <sup>-14</sup>	1.2 × 10 <sup>-14</sup>	5.2 × 10 <sup>-14</sup>	5.3 × 10 <sup>-14</sup>
PCO <sub>2</sub>	2.5 × 10 <sup>-14</sup>	2.8 × 10 <sup>-14</sup>	21.0 × 10 <sup>-14</sup>	21.3 × 10 <sup>-14</sup>
PH <sub>2</sub> O	0.6 × 10 <sup>-3</sup>	0.8 × 10 <sup>-3</sup>	5.7 × 10 <sup>-3</sup>	5.8 × 10 <sup>-3</sup>



From the results shown in the Table, it will readily be understood that when the coating layer is oriented, the organic solvent resistance, chemical resistance, hot water resistance, low-temperature burst characteristic and gas barrier properties are improved. The gas barrier properties obtained when the inner surface of the preform is coated is slightly superior to the gas barrier properties obtained when the outer surface of the preform is coated. The reason is believed to be that since the temperature at which the inner surface portion is drawn is lower than the temperature at which the outer surface portion is drawn, the heat history of the coating layer on the inner surface is reduced and deterioration is not caused. From the results of the measurement of the surface temperatures, it is expected that the temperature of the coating layer is lower by at least 10°C than the temperature of the resin substrate. It is construed that the reason why reduction of the properties of the coating layer on the outer surface is not significant is that since the temperature of the outer surface portion is rapidly lowered (it is expected that this temperature is reduced below the temperature of the resin substrate), deterioration is not caused.

#### Claims

1. A process for the preparation of coated oriented plastic vessels, which comprises coating an aqueous latex of a vinylidene chloride copolymer on at least one surface of a bottomed parison composed of amorphous polyethylene terephthalate, drying the coated latex to form a coated structure provided with a surface coating layer on a polyethylene terephthalate substrate and subjecting the coated structure to biaxial draw-blow-molding at a temperature at which the draw-molding of the coated structure is possible and draw-molding the coated structure at a temperature higher than the glass transition temperature of the vinylidene chloride copolymer but lower than the melting point of the vinylidene chloride copolymer to form the coated structure into a shape of a vessel while drawing the coating layer so that the coating layer of the vinylidene chloride copolymer has a molecular orientation, characterized in that the biaxial draw-blow-molding is carried out under conditions such that the temperature of the coating layer of the coated structure is lower by at least 5°C than the average temperature of the polyethylene terephthalate substrate and the resultant coating layer has a molecular orientation such that the sum of the two-dimensional orientation coefficients ( $l + m$ ) in the axial direction and circumferential direction is at least 0.03 as measured by polarised light fluorometry and the coating layer is not substantially peeled in the low-temperature burst test conducted at -5°C.
2. A process according to claim 1 wherein the aqueous latex has a solids content of 20 to 65% and a viscosity of 3 to 500 cps.

#### Patentansprüche

1. Verfahren zum Herstellen von beschichteten orientierten Kunststoffbehältern, wobei ein wäßriger Latex eines Vinylidenchloridcopolymer als Beschichtung auf mindestens eine Oberfläche eines mit einem Boden versehenen und aus einem amorphen Polyethylenterephthalat bestehenden Kübels aufgebracht wird, die Latexbeschichtung getrocknet wird, um eine beschichtete Struktur, die eine Oberflächenbeschichtung auf einem Polyethylenterephthalat-Substrat aufweist, zu bilden, und die beschichtete Struktur bei einer solchen Temperatur einer blaxialen Zieh-Blas-Formung unterworfen wird, bei der das Ziehformen der beschichteten Struktur möglich ist, und die beschichtete Struktur bei einer Temperatur ziehgeformt wird, die über der Glasübergangstemperatur des Vinylidenchloridcopolymer liegt, jedoch unterhalb des Schmelzpunkts des Vinylidenchloridcopolymer liegt, um die beschichtete Struktur in die Gestalt eines Behälters umzuformen, wobei die Beschichtung derart gezogen wird, daß sie oder das Vinylidenchloridcopolymer eine molekulare Orientierung aufweist, dadurch gekennzeichnet, daß das biaxiale Zieh-Blas-Formen unter solchen Bedingungen durchgeführt wird, daß die Temperatur der Beschichtung der beschichteten Struktur um mindestens 5°C unter der Durchschnittstemperatur des Polyethylenterephthalat-Substrats liegt und die erhaltene Beschichtung eine solche molekulare Orientierung aufweist, daß die Summe der Koeffizienten ( $l + m$ ) der zweidimensionalen Orientierung in der axialen Richtung und der Umfangsrichtung mindestens 0,03, gemessen durch Fluometrie mittels polarisiertem Licht, beträgt und in dem bei -5°C durchgeführten Tieftemperatur-Abschältest die Beschichtung im wesentlichen nicht abgeschält wird.
2. Verfahren nach Anspruch 1, worin der wäßrige Latex einen Feststoffgehalt von 20 bis 65% und eine Viskosität von 3 bis 500 cP aufweist.

#### Revendications

1. Procédé pour la préparation de récipients en matière plastique orientée, munis d'un revêtement, selon lequel on enduit d'un latex aqueux d'un copolymère de chlorure de vinylidène au moins une surface d'une paraison à fond composée de téréphthalate de polyéthylène amorphe, on sèche le latex enduit pour former une structure enduite munie d'une couche de revêtement de surface sur un substrat de téréphthalate de polyéthylène et on soumet la structure enduite à un moulage par soufflage-étrage biaxial à une température à laquelle le moulage par étrage la structure enduite est possible et mouler par étrage la structure ensuite à une température supérieure à la température de transition vitreuse du copolymère de

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chlorure de vinylidène mais inférieure au point de fusion du copolymère de chlorure de vinylidène pour donner à la structure enduite la forme, d'un récipient tout en étirant la couche d'enduction de manière que la couche d'enduction de copolymère de chlorure de vinylidène présente une orientation moléculaire, caractérisé par le fait que le moulage par soufflage-étirage biaxial est effectué dans des conditions telles  
5 que la température de la couche d'enduction de la structure enduite est inférieure d'au moins 5°C à la température moyenne du substrat de téréphtalate de polyéthylène et la couche d'enduction résultante à une orientation moléculaire telle que la somme des coefficients d'orientation bi-dimensionnelle ( $l + m$ ) en direction axiale et direction circonférentielle est d'au moins 0,03, tels que mesuré par fluorométrie en lumière polarisée et la couche d'enduction n'est pas sensiblement pelée dans l'essai d'éclatement à basse  
10 température, conduit à -5°C.

2. Procédé selon la revendication 1 dans lequel le latex aqueux a une teneur en solides de 20 à 65% et une viscosité de 3 à 500 cps.

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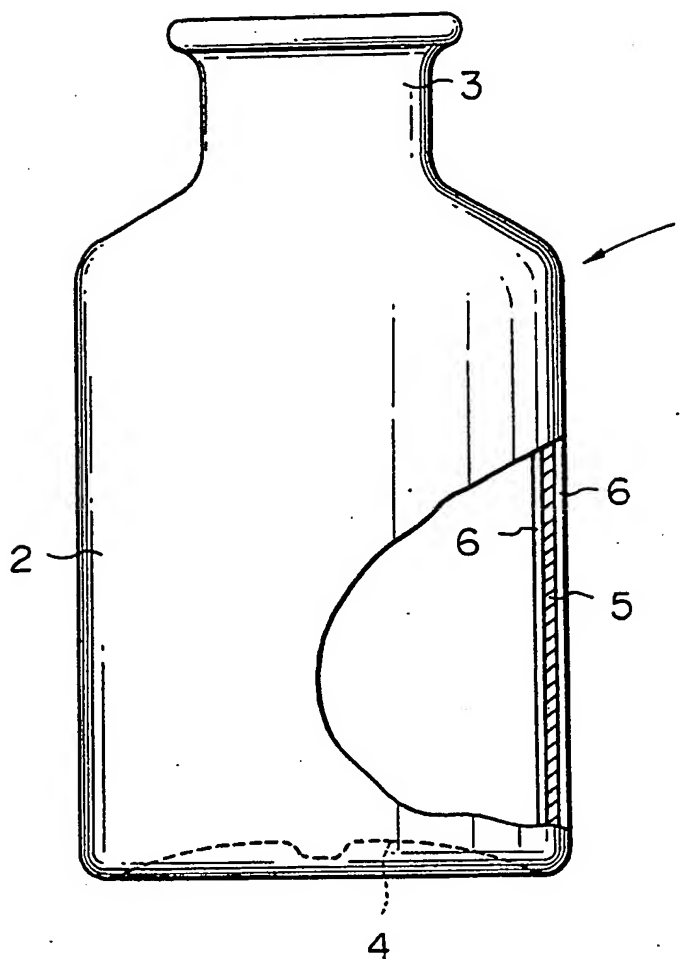
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*Fig. 1*



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